

Figure 3. Effect of thiourea on the titration of bismuth in the presence of copper; concentration of thiourea 0.02M, pH=1.2. Amount of copper: A 2mg, B 4mg, C 10mg, per gram of bismuth.

as shown in Figure 2. When thiourea is added to mask copper the end-point can be becomes sharper, but the results are

TABLE 3: Effect of Thiourea in the Presence of Copper

Bi taken g	Cu added mg	Bi found %	Deviation %	Remarks
1.12125	0	99.993	-0.007	Without thiourea
1.14255	0	100.000	0.000	Without thiourea
1.13584	0	100.001	+0.001	With thiourea
1.17175	0	99.997	-0.003	With thiourea
1.12212	2	99.993	-0.007	With thiourea
1.11930	4	99.989	-0.011	With thiourea
1.12214	6	99.936	-0.064	With thiourea
1.10240	10	99.929	-0.071	With thiourea

appreciably lower (Figure 3 and Table 3). From the data for pH=1.10 plotted in Figure 1, the formation constant of bismuth-EDTA complex (assuming 1:1 stoichiometry) is estimated to be 1.5×10^{24} at room temperature. Thus, the interference caused by the presence of copper ($pK_{MY}=18.8$) requires further study.

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Reaction of Thianthrene Cation Radical Perchlorate with N-Free and N-Alkylsulfonamides

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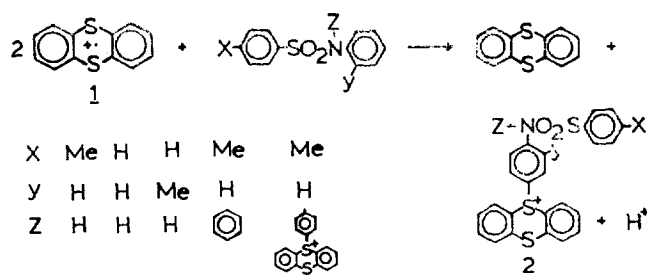
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Thianthrene cation radical perchlorate (1) reacted with N-free sulfonamides to give directly N-sulfonylsulfilimines (5a-5c) but reaction with N-alkylsulfonamides afforded, *inter alia*, 5-(2-thianthreniumyl) thianthrene perchlorate (6).

Introduction

In the previous paper,¹ we have shown that thianthrene cation radical perchlorate (1) reacted with N-arylbenzene- and N-aryl-*p*-toluenesulfonamides to give 5-(*p*-N-arylbzenesulfonamidophenyl)- and 5-(*p*-N-aryl-*p*-toluenesulfonamidophenyl) thianthrenium perchlorates (2) according to the following stoichiometry (Scheme 1).

This result indicates that a pair of nonbonding electrons on nitrogen atom of sulfonamides delocalizes into phenyl ring attached to nitrogen to cause the phenyl ring active although a sulfonyl group, *i. e.* a strong electron-withdrawing group is bonded to nitrogen.²



Scheme 1.

In order to understand further inherent electronic nature of nonbonding electrons on nitrogen, with the expectation

regarding either a nucleophilic attack of amino group to form a compound with structure such as $\text{>S}^+\text{-NHSO}_2^-$, which is analogous type of reactions of **1** with amines such as tert-butylamine and dimethylamine,³ or an electron transfer reaction between **1** and sulfonamide, which leads to the formation of thianthrene and sulfonamide cation radical, reactions of **1** with N-free and N-alkylsulfonamides were undertaken. We now report the results of these reactions.

Experimental

Thianthrene was obtained from Merck (Art. 821109) and was used without further purification and thianthrene cation radical perchlorate was prepared by the known method described previously¹.

Acetonitrile was Kanto Chemical Co. Extra pure and was refluxed with phosphorus pentoxide for 3 hr, followed by distilling twice and stored over molecular sieve (4Å, Merck, Art. 5708) in a septum capped bottle.

Methanesulfonyl chloride (Art. 806021) and benzenesulfonyl chloride (Art. 800470) were obtained from Merck. *p*-Toluenesulfonyl chloride was prepared using *p*-toluenesulfonic acid and phosphorus pentachloride, mp 68–70 °C (*lit.*⁴ 67.5–69 °C). *n*-Propylamine and benzylamine were obtained from Matheson Coleman & Bell. Benzenesulfonamide was obtained from Merck and used without further purification. *p*-Toluenesulfonamide was Kanto Chemical Co. Extra pure. Methanesulfonamide was prepared by bubbling ammonia gas in methanesulfonyl chloride in chloroform at an ice-water temperature, mp 91–92 °C (aq. ethanol, *lit.*⁵ 91–92 °C). *N*-*n*-Propyl-*p*-toluenesulfonamide was prepared by the addition of *n*-propylamine in *p*-toluenesulfonyl chloride in benzene, mp 49.5–50 °C (aq. ethanol, *lit.*⁶ 52 °C). *N*-Benzyl-*p*-toluenesulfonamide was prepared by the addition of *p*-toluenesulfonyl chloride in the mixture of benzylamine and 10% of KOH, followed by the addition of 25% HCl to cause the aqueous layer acidic (pH=4), mp 113–114 °C (aq. ethanol, *lit.*⁷ 114 °C).

Column chromatography was performed with Merck silica gel (Art 7734) and thin layer chromatography (t.l.c.) was carried out with Merck Kiesel 60 PF₂₅₄ gipshatig (Art 7749). Tlc plate was made by dipping the glass plate (3×8 cm) into the slurry in the mixture of methanol and chloroform (2:1, v/v). The chromatogram was visualized using mineral ultraviolet lamp (UVSL 25 Ultraviolet Products Inc. Gabriel, Calif., U.S.A).

Ultraviolet spectra were obtained using Beckmann UV-Vis spectrometer (Model 5260). Infrared spectra were obtained using Perkin-Elmer 283 Infrared Spectrometers and taken using potassium bromide pellets. ¹H nmr spectra were recorded using Varian EM 360A spectrometer and chemical shifts were measured in δ values using TMS as an internal standard.

All melting points were taken with Fisher-Johns melting point apparatus and are uncorrected. Elemental analyses were performed at Mic Anal Organic Microanalysis, Tucson, Arizona, U.S.A. Mass spectra were obtained from the

Research Institute of Industrial Sciences, College of engineering, S.N.U.

General Procedure. About 4mM of **1** and 9 mM of sulfonamide were placed in 100 ml round bottomed flask and dissolved in 25 ml of anhydrous acetonitrile. The flask was stoppered and wrapped with aluminum foil to prevent the mixture from a possible photoreaction. The mixture was stirred at room temperature until the dark purple color of the cation radical had disappeared completely. After the solvent was evaporated using rotary evaporator, the residue was chromatographed.

Thianthrene, thianthrene 5-oxide, and sulfonamide recovered were identified by comparison of ultraviolet spectrum and R_f value of each authentic compound.

Reaction of 1 with Methanesulfonamide. To a stirred solution of **1** (1.297 g, 4.10 mM) in 25 ml of acetonitrile was added methanesulfonamide (0.857 g, 9.41 mM). The dark purple color of the cation radical disappeared in 80 days and the color of the reaction mixture became pale red. Tlc (benzene) of the reaction mixture showed four spots, corresponding to thianthrene (**3**) ($R_f=0.67$), thianthrene 5-oxide (**4**) ($R_f=0.30$), an unknown ($R_f=0.12$), and an original spot. After the solvent was removed, the residue was chromatographed (1.9×13 cm).

Elution with hexane (50 ml×7) gave 0.501 g (2.32 mM) of **3**, while elution with benzene (50 ml×7) gave 0.080 g (0.34 mM) of **4**. Elution next with chloroform (50 ml×4) afforded 0.123g (0.40 mM) of pale yellow solid, which was recrystallized from ethanol-ether to give a white needle type crystal, identified as **5**, 5-dihydro-5-(*N*-methanesulfonyl)iminothianthrene (**5a**), mp 208–209 °C: $\lambda_{\text{max}}^{\text{EtOH}}$ (log ϵ) 228 (4.48), 287 (3.71) nm; IR (KBr) 1285, 1130 (SO₂ stretch), 990 (S–N–S asym. stretch) cm⁻¹; ¹H nmr (CDCl₃) δ 3.26 (s, 2H, methyl), 7.46–7.81 (m, 6H, 1, 2, 3, 7, 8, 9 positions of thianthrene ring), 7.82–8.20 (m, 2H, 4, 6 positions of thianthrene ring); MS m/e 309 (M⁺), 216 (B).

Elution with ethyl ether gave 0.817 (8.59 mM) of methanesulfonamide. Elution with acetone gave 0.997 g of yellowish brown sticky materials, which were washed with water to give about 0.212 g (0.40 mM) of yellow solids. The solids were dissolved in acetone and decolorized with charcoal. The white solid was recrystallized from acetonitrile, mp (dec) 145–151 °C; $\lambda_{\text{max}}^{\text{EtOH}}$ 317, 270, 229 nm; ¹H nmr (CDCl₃+DMSO-d₆) δ 6.86–7.97 (m, 13H, thianthrene ring and 1, 2, 3, 7, 8, 9 positions of thianthrene ring with trivalent sulfur atom), 8.41–8.70 (m, 2H, 4, 6 position of thianthrene ring with trivalent sulfur atom). Anal. Calcd. for C₂₄H₁₅ClO₄S₄: C, 54.28; H, 2.85; Cl, 6.68; S, 24.15. Found: C, 53.84; H, 2.84; Cl, 6.54; S, 24.33. This compound was assigned to be 5-(2-thianthreniumyl)thianthrene perchlorate (**6**).

Reaction of 1 with Benzenesulfonamide. To a stirred solution of **1** (1.02 g, 3.23 mM) in 20 ml of acetonitrile was added benzenesulfonamide (1.566 g, 9.96 mM). It took 90 days for the complete disappearance of the color of the cation radical. The reaction mixture showed four spots on the tlc plate (benzene) as in the reaction with methanesulfonamide.

The reaction mixture was worked up as before and the residue was chromatographed (1.9×12 cm).

Elution with hexane (50 ml×10) afforded 0.321 g (1.48 mM) of **3**, while elution with benzene (50 ml×8) gave 0.066g (0.28 mM) of **4**. Elution next with ethyl ether (50 ml×8) gave 1.337g (8.51 mM) of benzenesulfonamide. Elution with acetone gave 1.973 g of sticky materials, which were recrystallized from a mixture of ethanol and small amount of ethyl ether to give 0.316 g (0.85 mM) of a white crystal, identified as 5,5-dihydro-5-(N-benzenesulfonyl)iminothianthrene (**5b**), mp 232–234 °C; $\lambda_{\text{max}}^{\text{EtOH}}$ (log ϵ) 227 (4.23), 287 (3.00) nm; IR (KBr) 1312, 1150 (SO₂ stretch), 1086, 970(S–N–S asym. stretch) cm⁻¹; ¹H nmr (DMSO-d₆) δ 7.43–7.75(m, 11H, aromatic), 7.75–8.10 (m, 2H, 4, 6 positions of thianthrene); MS m/e 371 (M⁺), 230 (B). The remainder was treated with a mixture of acetonitrile and ether to give 0.186 (0.35 mM) of **6**.

Reaction of 1 with p-Toluenesulfonamide. To a stirred solution of **1** (1.299 g, 4.11 mM) in 28 ml of acetonitrile was added *p*-toluenesulfonamide (1.360 g, 7.94 mM). The reaction was completed in 40 days. The reaction mixture showed five spots on the tlc plate, corresponding to **3**, **4**, *p*-toluenesulfonamide (*R_f*=0.10), and two unknowns (*R_f*=0.15, 0). Column chromatography (1.9×13 cm) of the reaction mixture using hexane and benzene gave 0.489 g (2.26 mM) of **3**, 0.070g (0.30 mM) of **4**, respectively. Elution with ethyl ether (50 ml×5) gave 1.539 g of mixture of *p*-toluenesulfonamide and an unknown (*R_f*=0.15). Addition of 2 ml of ethanol to the mixture gave 0.39g (0.86 mM) of a white solid, which was recrystallized from aq. ethanol to give crystals, identified as 5,5-dihydro-5-(N-*p*-toluenesulfonyl)iminothianthrene (**5c**), mp 170–171 °C (*lit.*⁸ 172–173 °C); $\lambda_{\text{max}}^{\text{EtOH}}$ 230, 286 nm; IR (KBr) 1310, 1141 (SO₂ stretch), 1090, 960 (S–N–S asym. stretch) cm⁻¹; ¹H nmr (CDCl₃) δ 2.40 (*s*, 3H, methyl), 7.19–7.68 (*m*, 10H, aromatic), 7.70–8.20 (*m*, 2H, 4, 6 positions of thianthrene).

Elution with acetone gave 1.156g of yellowish brown sticky materials, which were washed with water to give 0.340g of yellow solids. The solid was recrystallized from acetonitrile to give 0.216g (0.41 mM) of **6**.

Reaction of 1 with N-n-Propyl-p-toluenesulfonamide. To a stirred solution of **1** (1.554g, 4.92 mM) in 30 ml of acetonitrile was added N-*n*-propyl-*p*-toluenesulfonamide (2.123g, 9.95 mM). The reaction was completed in 180 days and color of the reaction mixture was dark brown. The reaction mixture indicated only the presence of **3**, N-*n*-propyl-*p*-toluenesulfonamide, and an unknown (*R_f*=0) on the tlc plate (benzene). The reaction mixture was worked up as usual and the residue was chromatographed (1.9×20 cm).

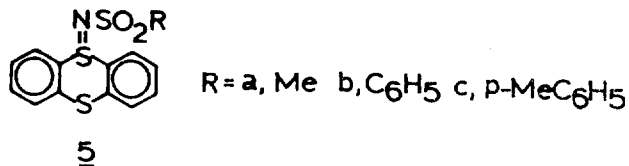
Elution with hexane (50 ml×13), gave 0.236 g (1.09 mM) of **3**. Elution with benzene (50 ml×2) gave 0.012g (0.05 mM) of **4**. The rest of benzene fractions (50 ml×8) gave 2.094 g (9.82 mM) of excess N-*n*-propyl-*p*-toluenesulfonamide. Finally elution with acetone (50 ml×6) gave 1.880 g of dark brown sticky materials, which were treated with water and 0.710g (1.34 mM) of brown solids were obtained. All spectral data and mp of these solids were consistent with those of **6**.

Reaction of 1 with N-benzyl-p-toluenesulfonamide. To a stirred solution of **1** (1.225g, 3.88 mM) in 20 ml of acetonitrile was added N-benzyl-*p*-Toluenesulfonamide (1.927g, 7.37 mM). Color of the cation radical disappeared in 90 days. The reaction mixture showed three spots on the tlc plate (benzene), corresponding to **3**, sulfonamide, and an unknown (*R_f*=0) and was worked up as usual.

Elution with hexane (50 ml×7), followed by toluene (50 ml×4) gave 0.269g (1.24 mM) of **3** and 0.007g (0.03 mM) of **4**, respectively. Elution next with benzene (50 ml×8) gave 1.816g (6.95 mM) of N-benzyl-*p*-toluenesulfonamide. Finally elution with acetone (50 ml×3) gave 1.535 g of dark brown sticky materials, which were treated with water to give 0.585g (1.10 mM) of yellow solids of which spectral data were in good agreement with those of **6**.

Results

The reaction with N-free sulfonamides such as methane-, benzene-, and *p*-toluenesulfonamide, *inter alia*, afforded directly the corresponding sulfilimines, *i.e.*, 5,5-dihydro-5-(N-methanesulfonyl)iminothianthrene (**5a**), 5,5-dihydro-5-(N-benzenesulfonyl)iminothianthrene (**5b**), and 5,5-dihydro-5-(N-*p*-toluenesulfonyl)iminothianthrene (**5c**).



The only other products were thianthrene (**3**), a small amount of thianthrene 5-oxide (**4**), which could be formed from the reaction of **1** with water remained in the solvent, and 5-(2-thianthreniumyl) thianthrene perchlorate (**6**). The following Table 1 summarizes the amounts of reactants and products. In the meantime, the reaction of **1** with N-alkylsulfonamides afforded **6** as a major product along with **3** and a small amount of **4** as usual as shown in Table 2.

It took 180 and 90 days for N-propyl and N-benzyl derivatives, respectively for the completion of the reactions and all the sulfonamides were essentially recovered. In these

TABLE 1: Summary of the Reaction of **1** with RSO₂NH₂

Reactants (mM)		Products (mM)				
1	R	3	4	5	6	R*
4.10	CH ₃ , 9.41	2.32	0.34	a, 0.40	0.40	8.59
3.23	C ₆ H ₅ , 9.96	1.48	0.28	b, 0.85	0.35	9.01
4.11	<i>p</i> -CH ₃ C ₆ H ₄ , 7.94	2.26	0.30	c, 0.86	0.41	6.69

R*: recovered sulfonamides

TABLE 2: Summary of the reaction of **1** with CH₃C₆H₄SO₂NHR

Reactants (mM)		Products (mM)				
1	R	3	5	6	R*	
4.92	CH ₃ CH ₂ CH ₂ , 9.95	1.09	0.05	1.34	9.82	
3.88	C ₆ H ₅ CH ₂ , 7.37	1.24	0.03	1.10	6.95	

cases, the sulfonamides did not act as nucleophiles.

Discussion

Several methods for the preparation of sulfilimines are now known.^{7,10} Recently,³ as the first example for the preparation of N-alkylsulfilimine using cation radical has been reported the reaction of **1** with tert-butylamine from which 5-(tert-butylimino)-5,5-dihydrothianthrene was isolated by treating the sulfonium salt with 30% NaOH. To our knowledge, isolation of **5a-5c** from the reaction with N-free sulfonamides is the first example for the preparation of N-sulfonylsulfilimines from cation radical.

Of N-sulfonylsulfilimines (**5a-5c**), **5c** is the only known compound.⁸ The structure of the other sulfilimines is inferred from the spectroscopic data (Table 3): Arenesulfonylsulfilimines show generally four characteristic bands at 1280-1260, 1140-1130, 1090-1070, and 1012-930cm⁻¹, representing SO₂ stretching vibrations for the first two and the asymmetric S^N-N-S^N band for the lowest frequency.⁹ Table 3 shows that the observed IR data are in good agreement with the values described above.

It has been known⁸ that many arenesulfonylsulfilimines show two characteristic maxima in the ultraviolet region, one close to 230nm (log ε, 4.0-4.5) and the other near 270 nm (log ε, 3.0-4.5). In particular, the absorption close to 230 nm has been interpreted to mean that the ylene structure makes a contribution to sulfilimine bonding.¹¹ These absorption properties are quite consistent with the values in Table 3 and indicate the importance of the ylene structure of the sulfilimines.

¹H nmr signal representing two protons close to 8 ppm indicates the semi-polar nature of the sulfur-nitrogen bond in sulfilimines. That is, the formation of the positive charge on sulfur (IV) causes down field chemical shift of protons at C-4 and C-6 of thianthrene ring. Analogous results have been obtained from 5-substituted thianthrenium perchlorates or thianthrene 5-oxide.¹² Therefore, not only ylene structure but also ylide structure contribute to the bond representation.

The compound **6** has been obtained from different reactions. The first isolation was achieved by stirring of **1** in acetonitrile for a long period at room temperature.¹³ The compound was characterized with ¹H nmr, IR, and UV data along with the result of elemental analysis. The second method with an

advantage of a short reaction time was to reflux a mixture of **1** and a radical initiator such as benzoyl peroxide¹⁴ or azobisisobutyronitrile (AIBN)¹⁵ in acetonitrile. That is, refluxing of 2.84 mM of **1** and 15.7 mM of benzoyl peroxide in 40 ml of acetonitrile for 1.5 hr was resulted in complete color change to bright orangish solution and afforded 1.02 mM of **6**. Time for the color change of **1** increases with decreasing the concentration ratio of benzoyl peroxide to **1**. Analogous result was obtained from the reaction with AIBN only when the concentration ratio of AIBN to **1** was not beyond the certain value. For instance, refluxing of 5.40 mM of **1** and 20.0 mM of AIBN in 40 ml of acetonitrile did not give **6**, while 5.28 mM of **1** and 5.90 mM of AIBN gave 0.457 mM (purified yield) of **6** at the same temperature. Yield of **6** increased with the concentration ratio of **1** to AIBN. One interesting observation is that in either reaction, no coupling product between **1** and a radical has been isolated. In the meantime, **6** (2.02 mM, purified yield) was formed simply by refluxing **1** (4.7 mM) itself in 40 ml acetonitrile for 48 hr.

Recently,¹⁶ we have found that **6** can be obtained in 63% yield by refluxing **1** (4.75 mM) and **3** (6.94 mM) in 40 ml acetonitrile for 24 hr.

It is not known whether **6** is formed by nucleophilic attack of **3** to thianthrene dication or by the coupling of two molecules of **1**.

Although the formation of sulfilimines (**5a-5c**) can analogously be explained by the mechanism of the formation of N-(tert-butylamino)thianthrenium perchlorate which led directly to N-(tert-butylimino)-5,5-dihydrothianthrene by treatment with strong base,³ the half-regeneration mechanism can not be ruled out.¹²

One contrastive thing of the reaction with N-free sulfonamide to that with tert-butylamine is that N-(alkane- or arene-sulfonyl)thianthrenium perchlorates which are analogous to N-(tert-butylamino)thianthrenium perchlorate have not been isolated.

In order to see if protonation of **5b** occurs, was added a drop of either conc. hydrochloric acid or 70% perchloric acid to an ethanolic solution of **5b** in a cuvette and recorded UV spectrum. However, no spectral change was recorded. This observation suggests that N-sulfonylsulfilimines are too weak bases to be protonated by the acids mentioned. Therefore, it is expected that as soon as N-(alkane- or arenesulfonyl)thianthrenium perchlorates are formed, they undergo rapidly deprotonation reactions to give sulfilimines.

In the cases of the reaction with N-propyl- and N-benzyl-sulfonamides, only **6** was obtained as a major product and fonamide was essentially recovered. Inertness of N-alkylsulfonamides used may be due to steric bulk around nitrogen atom because nonbonding electron density on nitrogen atom of N-alkylsulfonamides is expected slightly greater than that of N-free sulfonamides. We have not yet tried the reaction with sulfonamides with N-methyl group which is the smallest alkyl group.

Acknowledgement. We are grateful to the Research

TABLE 3: Spectral Characteristic of Sulfilimines

Sulfilimines	IR, cm ⁻¹	¹ H nmr, δ	λ _{max} ^{EtOH} (log ε)	MS m/e (M ⁺)
5a	1285	3.26 (s, 3H, Me)	228 (4.48)	309
	1130	7.46-7.81 (m, 6H, aromatic)	287 (3.71)	
	990	7.82-8.20 (m, 3H, aromatic)		
	1312	7.43-7.75 (m, 11H, aromatic)	227 (4.23)	
5b	1150	7.75-8.10 (m, 2H, aromatic)	287 (3.00)	371
	1086			
	970			

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Molecular Dynamics Study of the Self-Diffusion Coefficient and Velocity Autocorrelation Function of a Polymer Molecule in Solution

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A molecular dynamic computer experiment was performed on a system of 108 particles composed of a single polymer chain and solvent molecules. The state considered was in the immediate neighborhood of the triple point of the system. The polymer itself is an analog of a freely jointed chain. The Lennard-Jones potential was used to represent the interactions between all particles except for that between the chain elements forming a bond in the polymer chain, for which the interaction was expressed by a harmonic potential. The self-diffusion coefficient and velocity autocorrelation function (VACF) of a polymer were calculated at various chain lengths N_p and various interaction strengths between solvent molecules and a polymer chain element. For self-diffusion coefficients D , the Einstein relation holds good; as chain length N_p increases the D value decreases, and D also decreases as ϵ_{cs} (the interaction parameter between the chain element and solvent molecules) increases. The relaxation time of velocity autocorrelation decreases as ϵ_{cs} increases, and it is constant for various chain lengths. The diffusion coefficients in various conditions reveal that our systems are in a free draining limit as is well known from the behavior of low molecular weight polymers, this also agrees with the Kirkwood-Riesman theory.

Introduction

There have been extensive studies by a molecular dynamic method on diffusion phenomena and on the behavior of velocity autocorrelation functions of pure liquids¹⁻⁵ and of a system of a structure-less particle immersed in solvent.⁶⁻⁸ These computational results can be compared with theories developed well, for example, the Enskog-Chapman theory⁹ and theory of Brownian motion.¹⁰ In addition, these computer experiments revealed new phenomena, for example, a negative tail¹ and slowly decaying motion of velocity autocorrelation function,²⁻⁵ which were soon theoretically explained.¹¹

But in case of polymeric systems there has been less study

because the potential forms of various configurational states of a polymer are not exactly known, and the theories are quite complicated.

Recently several authors simulated a single polymer chain immersed in solvent by the Monte Carlo method¹²⁻¹⁴ and molecular dynamic method,¹⁵⁻¹⁶ assuming simple potentials between particles almost just as in the case of simple liquids and also assuming simple models for the polymer molecule. These studies revealed many interesting results which are reasonable in view of the behavior of real polymer solutions in spite of the simplicity of models adopted.

In contrast to the results on simple liquids, the results of the two methods for polymer systems do not always give rise to the same results. This is because in the Monte Carlo